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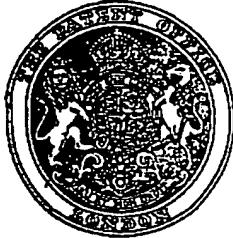
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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Recovery of Aliphatic Acids from the Oxidation Products of Hydrocarbons

We, THE DISTILLERS COMPANY LIMITED, a British Company, of 12, Torphichen Street, Edinburgh, 3, Scotland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

The present invention relates to a process for the production of pure formic and acetic acids.

It is an object of the present invention to facilitate the separation by distillation of acetic and formic acids from the oxidation products of paraffinic hydrocarbons, for example the lower paraffins. It is a further object to separate these acids, either together or separately, in a high degree of purity.

The oxidation products to which the process of our invention may be applied are obtained, for example, in the liquid phase oxidation of lower paraffins as described in our Specifications Serial Nos. 743,989, 743,990 and 743,991, and in copending British Applications Nos. 1051/53 and 11469/53 (Serial Nos. 25 771,991 and 767,290).

The components of the liquid oxidation product obtained may be classified as (a) volatile non-acidic oxidation products of boiling point up to 99° C. in the presence of water, herein-after referred to as "light ends", (b) water, (c) aliphatic monocarboxylic acids of 1 to 4 carbon atoms and (d) higher boiling residues, including higher acids. The relative proportions of these components (a)–(d) may vary widely, depending on the oxidation feedstock and conditions, without affecting the process of the invention.

When such a liquid oxidation product is subjected to a normal fractional distillation, then after the light ends and water preferably with the aid of an entrainer have distilled over, the monocarboxylic acids of 1–4 carbon atoms can be distilled over as successive fractions. As formic and acetic acids are difficult to separ-

ate from each other by distillation, they are 45 subjected to a further operation to separate the two components. No matter how carefully the separation of the "light ends" is carried out during this fractional distillation of the oxidation product, the formic acid and acetic acid 50 fractions are, or the mixed formic-acetic acid fraction is, found to be contaminated by impurities which may impart a colour and foreign odour and which also may be detected by analytical methods, for example those used 55 to detect the presence of carbonyl and ester groups.

It has been found that if the mixture of water and acids of 1 to 4 carbon atoms is separated from the higher boiling residues, 60 prior to dehydration and fractionation to separate the individual acids, there is a considerable improvement in the purity of the formic acid-acetic acid fraction obtained.

Accordingly, the present invention is for a 65 process for the recovery of formic and acetic acids from the product of the liquid phase oxidation of paraffinic hydrocarbons with a gas comprising molecular oxygen, said product containing (a) light ends, as hereinbefore 70 defined, (b) water, (c) aliphatic monocarboxylic acids of 1 to 4 carbon atoms and (d) higher boiling residues, which comprises distilling the product desirably from which all or part of the light ends have been removed to separate from 75 the higher boiling residues a distillate mixture comprising water and the aliphatic monocarboxylic acids of 1 to 4 carbon atoms and thereafter fractionally distilling this mixture, after removal of any remaining light ends, to 80 recover the formic and acetic acids.

During this distillation of the oxidation product small amounts of volatile, coloured, non-acidic materials boiling up to 99° C. in the presence of water, for example ketones and esters 85 are produced, probably as a result of the decomposition or oxidation of components of the residues. These non-acidic substances co-

distil with the mixture of water and mono-carboxylic acids of one to four carbon atoms, and are hereinafter referred to as "subsidiary light ends". Hence, although the separated formic and acetic acids fraction subsequently obtained is of improved purity compared with that obtained by the known method of straight fractional distillation, there may still be found amounts of volatile impurities in the formic acid-acetic acid fractions obtained. While the presence of these impurities may be tolerated in some applications of the acids, for many applications these impurities cannot be tolerated since they may impart an undesirable colour or they may show a tendency to oxidise and thus to contaminate the acids of the products into which the acids may be converted. More particularly in the case of acetic acid fractions there may be produced an unacceptable residual odour after neutralisation or the acid may otherwise fail to conform to the stringent industrial specifications.

It has further been found that these remaining undesirable impurities may be eliminated or reduced to negligible proportions by subjecting the mixture of water and acids to a further distillation operation, following its separation from the light ends and residues, in which the mixture is fractionally distilled to remove as distillate the subsidiary light ends. Upon subsequent separation of the formic and acetic acids from the base product of this last distillation, for instance by removal of water followed by fractional distillation, we have found that a formic acid-acetic acid fraction may be obtained which is virtually colourless and free from ester or carbonyl impurities and further that there may be isolated from this fraction, or from the mixed C₁ to C₄ acids after removal of water, a pure acetic acid which satisfies the most stringent industrial requirements and has little or no residual odour after neutralisation.

Accordingly, a preferred embodiment of the present invention comprises the steps in the separation of pure fractions of formic acid and acetic acid from the product of the liquid phase oxidation of paraffinic hydrocarbons with a gas comprising molecular oxygen, of distilling the oxidation product, desirably from which all or part of the light ends have already been removed, so as to separate a mixture of water and aliphatic monocarboxylic acids of 1 to 4 carbon atoms from the higher boiling residues, and then subjecting this mixture to fractional distillation to remove as distillate subsidiary light ends boiling up to 99° C. in the presence of water, prior to separating the formic acid-acetic acid fraction by fractional distillation of the residue.

The separation of the mixture of water and the aliphatic acids of 1 to 4 carbon atoms from the residues may, for example, be carried out by flash distillation without fractionating, or preferably with the provision of a certain degree of fractionation by means of a frac-

tionating column and reflux. The separation may be carried out either under reduced pressure or at atmospheric pressure. The residues from this distillation may be oxidised or recycled to the oxidation stage as for example 70 is described in British Application No. 11469/53 (Serial No. 767,290).

It has generally been found desirable in this distillation to restrict the temperature of the still base to about 160° C. In this case it may 75 be advisable to operate under vacuum to obtain maximum stripping of acids.

The preliminary distillation of the oxidation product may be carried out so as to remove only part of the volatile products as the light 80 ends fraction, the remainder being removed together with the subsidiary light ends.

If so desired, the distillate comprising the subsidiary light ends may be allowed to separate into two liquid phases, which may be 85 separated so that all or part of the upper liquid phase is removed, any remainder of this upper liquid phase being returned to the still as reflux; and all or part of the lower liquid phase is returned to the still as reflux, any remainder 90 being removed. Of the two distillate liquid phases, the upper phase contains the bulk of the impurities whose removal from the acids is one of the objects of our invention; these impurities however may with advantage be 95 recycled to the oxidation stage. The lower liquid phase of the distillate is mainly water, and part or all of this may desirably be returned to the still as reflux while any remainder is removed from the system since in 100 this way a certain degree of dehydration may be achieved. It is important, however, that there should at all times be a sufficient concentration of water in the base of the still at this stage to ensure complete removal of the impurities, 105 and any dehydration effected should not be carried out so as to reduce the concentration of water in the base product to below about 8—10% by weight.

The following examples are given to illustrate the process of the present invention:—

EXAMPLE 1.

An oxidation product, obtained by the liquid phase oxidation at 160° C. and at a pressure of 300 pounds per square inch gauge of a paraffinic hydrocarbon fraction of boiling range 115 15°—95° C. prepared by the straight distillation of a Middle-East petroleum was fractionally distilled to remove completely the light ends boiling up to 99° C. in the presence of 120 water. The base product from this distillation was freed from the higher boiling compounds by distillation through a fractionating column packed with glass helices and equivalent to about 8 theoretical plates, at a reflux ratio of 125 1:1. The crude mixture of water and the C₁ to C₄ acids thus obtained was subjected to a further fractional distillation through a packed column up to a head temperature of 99° C. at

atmospheric pressure which produced a further 1.0% by weight approximately of subsidiary light ends, substantially neutral material of a bright yellow colour, which distilled over as a heteroazeotrope with water containing a small amount of acid. After removal of these impurities the remainder was fractionated through a column packed with glass helices, first in the presence of isopropyl ether to remove water and then to separate a formic acid-acetic acid fraction, boiling at 100° to 119° C. at 760 mm. mercury pressure. The formic acid-acetic acid fraction thus obtained was almost colourless and contained by analysis the following amounts of impurities:—

Ester—0.2 milliequivalents per 100 grams
Carbonyl compounds—0.2 milliequivalents per 100 grams.

EXAMPLE 2.

An oxidation product prepared by oxidising the same feedstock as was used in Example 1 at 170° C. and a pressure of 600 pounds per square inch gauge, was fractionally distilled to remove the light ends boiling up to 99° C. in the presence of water as completely as possible. The base product from this distillation was freed from the higher boiling components by distillation through a fractionating column packed with glass helices and equivalent to about 18 theoretical plates, at a reflux ratio of 1:1. The crude mixture of water and C₁ to C₄ acids thus obtained was subjected to a further fractional distillation through a packed column to a head temperature of 99° C. at atmospheric pressure which produced a further 1.5% by weight of substantially neutral materials of a yellow colour distilling over as a heteroazeotrope with water containing a small amount of acid. After removal of these impurities, the remainder was fractionated up a column packed with glass helices, first in the presence of isopropyl ether to remove water and then to separate a formic acid-acetic acid fraction, boiling at 100° to 119° C. at 760 mm. mercury pressure. The pure formic acid-acetic acid fraction thus recovered was colourless and contained no detectable ester or carbonyl impurity.

EXAMPLE 3.

An oxidation product prepared by oxidising the same feedstock as was used in Example 1 at 170° C. and a pressure of 600 pounds per square inch gauge, was fractionally distilled in a continuous still at atmospheric pressure to remove the more volatile light ends, the head temperature being 60—65° C. The still base product was distilled at atmospheric pressure from higher boiling material in a continuous still of about 30 theoretical plates with fractionation, the head temperature being about 100—110° C. In order to remove subsidiary light ends, the crude mixture containing water and C₁ to C₄ acids thus obtained was fed to the mid-point of a continuous distillation column of 30 theoretical plates, under a reflux

ratio of 7:1, the column head temperature 65 being about 95° C and the total distillate about 12% of the feed. The still base product from this distillation column was dehydrated using isopropyl ether as the entrainer in a continuous still, and the dehydrated acids thus obtained were fractionally distilled in a batch still to recover the formic-acetic acid fraction, boiling at 100° to 119° C. at 760 mm. mercury pressure. The formic acid-acetic acid fraction was colourless and contained no detectable ester or carbonyl impurity. 75

EXAMPLE 4.

The apparatus employed in the process of this example is shown diagrammatically in the accompanying drawing. An oxidation product, 80 obtained by the liquid phase oxidation at 170° C. and at a pressure of 600 pounds per square inch gauge, of a paraffinic hydrocarbon fraction of boiling range 15 to 95° C. prepared by the straight distillation of a Middle East petroleum, was introduced by line (1) into a continuous still (2) operated at a head temperature of about 60°—65° C. From the head of the still the volatile light ends were removed by line (3), and from the base of the still, the base 90 product comprising the acids were removed by line (4) and applied to a continuous still (5) of 5 to 7 theoretical plates wherein the base product was fractionally distilled to separate the crude mixture of acids from the higher boiling material, the column being operated at a head temperature of about 100—110° C. The higher boiling residues were taken off by line (6), and the distillate comprising the aqueous C₁ to C₄ aliphatic acids was taken off by line 100 (7) and fed to a continuous distillation column (8) of approximately 15 theoretical plates, the reflux ratio being about 9:1 and the head temperature 90 to 95° C., the total distillate being about 10% of the feed. The distillate comprising subsidiary light ends, was passed by line 105 (9) to a phase separator (10) where the distillate separated into two phases, all or part of the lower liquid phase and/or part of the upper liquid phase being returned to the still as 110 reflux, the remainders being removed. The base product, comprising the aqueous acids, was removed by line (11) and passed to a continuous dehydrating still (12) using isopropyl ether as entrainer. The overheads from the 115 column were taken to a phase separator (13), the separated isopropyl ether layer returned to the column and the water removed. The still base product, comprising the dried acids, was passed by line (14) to a continuous still (15) 120 using toluene as entrainer in the still (15). The overheads from the column were taken to a phase separator (16), the lower layer comprising formic acid being taken off and the upper layer comprising toluene being returned to the 125 column. The still base product was passed by line (17) to a continuous fractionation still (18) to separate as the overheads by line (19) acetic

acid, which was finally distilled to remove traces of toluene and formic acid. The still base product removed by line (20) comprised the higher, i.e. C_3 and C_4 aliphatic acids. The 5 acetic acid thus obtained was completely colourless, contained no detectable amounts of esters or ketonic compounds and completely satisfied the requirements of British Standard Specification, B.S. No. 576:1950.

10 By way of comparison a sample of the aqueous oxidate as used in Example 1 was fractionated in a fractionating column of about 15 theoretical plates packed with glass helices. The formic acid-acetic acid fraction of boiling 15 point range 100°—127° C./60 mm. mercury was brown in colour and contained the following amount of impurities:—

Ester—16 milliequivalents per 100 grams.

15 Carbonyl compounds—17 milliequivalents 20 per 100 grams.

After neutralisation with alkali a strong residual odour of higher ketones and esters remained.

In the examples of our British Specifications 25 Serial Nos. 743,989, 743,990 and 743,991, and our co-pending Application 1051/53 (Serial No. 771,991) are described processes in which lower paraffins are oxidised in the liquid phase to produce lower aliphatic acids, and in which 30 the oxidation product is distilled to recover a mixture of acids of 1 to 4 carbon atoms and water. The claims of the present application are to be read as not including anything claimed in the claims to those examples of 35 these British specifications in which the recovery of formic and acetic acids by the separation of a fraction comprising a mixture of C_1 to C_4 acids and water, followed by the fractional distillation of this fraction to recover 40 formic and acetic acids is described, and in those claims of co-pending Application No. 1051/53 (Serial No. 771,991) which also include this recovery step.

Subject to the foregoing disclaimer what we 45 claim is:—

1. A process for the recovery of formic and acetic acids from the product of the liquid phase oxidation of paraffinic hydrocarbons with

a gas comprising molecular oxygen, said product containing (a) light ends, as hereinbefore defined, (b) water, (c) aliphatic monocarboxylic acids of 1 to 4 carbon atoms and (d) higher boiling residues, which comprises distilling the product desirably from which all or part of the light ends have been removed, to 55 separate from the higher boiling residues a distillate mixture comprising water and the aliphatic monocarboxylic acids of 1 to 4 carbon atoms and thereafter fractionally distilling this mixture after removal of any remaining light 60 ends, to recover the formic and acetic acids.

2. A process according to Claim 1 wherein the mixture containing water and the aliphatic monocarboxylic acids of 1 to 4 carbon atoms is first distilled to remove as distillate subsidiary 65 light ends, as hereinbefore defined, while the concentration of water in the base of the still is maintained above about 8—10%, and thereafter the base product is fractionally distilled 70 to recover the formic and acetic acids.

3. A process according to Claim 1 or 2 wherein at least a portion of the light ends is separated by distillation prior to said distillation process for separating the mixture containing water and the aliphatic monocarboxylic 75 acids of 1 to 4 carbon atoms.

4. A process according to any of the preceding claims wherein the mixture comprising water and the aliphatic monocarboxylic acids of 1 to 4 carbon atoms is separated from the higher boiling residues by 80 flash distillation.

5. A process according to any of the Claims 1—3, wherein the mixture of water and aliphatic carboxylic acids of 1 to 4 carbon atoms is separated from the higher boiling residues by 85 distillation under vacuum at a still base temperature of about 160° C.

6. A process for the recovery of formic and acetic acids substantially as described in any of the examples.

7. Formic acid when prepared by the process of any of the preceding claims.

8. Acetic acid when prepared by the process of any of the preceding claims.

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PROVISIONAL SPECIFICATION

Recovery of Aliphatic Acids from the Oxidation Products of Hydrocarbons

95 We, THE DISTILLERS COMPANY LIMITED, a British Company, of 12, Torphichen Street, Edinburgh, 3, Scotland, do hereby declare this invention to be described in the following statement:—

100 The present invention relates to a process for the production of pure formic and acetic acids.

105 It is an object of the present invention to facilitate the separation by distillation of acetic and formic acids from the oxidation products of hydrocarbons, for example the lower para-

fins. It is a further object to separate these acids, either together or separately, in a high degree of purity.

The oxidation products to which the process 110 of our invention may be applied are obtained, for example, in the liquid phase oxidation of lower paraffins as described in our co-pending Applications Nos. 25789/52, 25792/52, 25794/52, 1051/53 and 11469/53. The components of the liquid oxidation product obtained may be classified as (a) volatile non-acidic oxidation products of boiling point up 115

to 99° in the presence of water ("light ends"), (b) water, (c) aliphatic monocarboxylic acids of 1 to 4 carbon atoms and (d) higher boiling residues (including higher acids).

5 When a liquid oxidation product is subjected to a normal fractional distillation, then after removal by distillation of "light ends" (as defined above) and water (preferably with the aid of an entrainer), the monocarboxylic acids of 1-4 carbon atoms may be distilled over as successive fractions. As formic and acetic acids are difficult to separate by distillation, they are usually recovered as a single mixed fraction which is subjected to a further operation to separate the two components. No matter how carefully the separation of the "light ends" is carried out during this fractional distillation of the oxidation product, the formic acid and acetic acid fractions, or the 10 mixed formic-acetic acid fraction, is found to be contaminated by impurities which may impart a colour and foreign odour and which also may be detected by analytical methods, for example those used to detect the presence 15 of carbonyl and ester groups.

It has been found that if the mixture of acids of 1 to 4 carbon atoms and water is separated from the residues, prior to dehydration and fractionation to separate the individual acids, 20 there is a considerable improvement in the purity of the formic acid-acetic acid fraction obtained.

Accordingly, the present invention comprises the step in the separation of pure fractions of formic acid and acetic acid from the oxidation product of lower hydrocarbons by distilling the oxidation product so as to separate a mixture of water and the lower aliphatic 25 monocarboxylic acids of not more than 4 carbon atoms from the higher boiling residues and thereafter fractionating this mixture.

During the distillation from the residues, as described, small amounts of volatile, coloured, non-acidic materials (for example ketones and 30 esters) are produced, probably as a result of the decomposition or oxidation of components of the residues, and these non-acidic substances co-distil with the mixture of water and monocarboxylic acids of one to four carbon atoms. Hence, although the separated formic and 35 acetic acids fraction so obtained is of improved purity compared with that obtained by the known method of straight fractional distillation, there may still be found amounts of volatile 40 impurities in the formic acid-acetic acid fractions obtained. While the presence of these impurities may be tolerated in some applications of the acids, for many applications these impurities cannot be tolerated since they may 45 impart an undesirable colour or they may show a tendency to oxidise and thus to contaminate the acids or the products into which the acids may be converted. More particularly in the case of acetic acid fractions there may be produced an unacceptable residual odour after

neutralisation or the acid may otherwise fail to conform to the stringent industrial specifications.

It has further been found that these remaining undesirable impurities may be eliminated or reduced to negligible proportions by subjecting the mixture of water and acids to a further distillation operation following the separation from the residues in which the mixture is fractionally distilled to remove as distillate the material which in the presence of water is more volatile than formic and acetic acids. Upon subsequent separation of these acids from the base product of this last distillation, for instance by removal of water followed by fractional distillation, we have found that a formic acid-acetic acid fraction may be obtained which is virtually colourless and free from ester or carbonyl impurities; and further that there may be isolated from this fraction, or from the mixed acids after removal of water, a pure acetic acid which satisfies the most stringent industrial requirements and has little or no residual odour after neutralisation.

Accordingly, the preferred embodiment of the present invention comprises the steps in the separation of pure fractions of formic acid and acetic acid from the oxidation products of lower paraffins, of distilling the oxidation product, desirably from which the volatile non-acidic products have already been removed, so as to separate a mixture of water and aliphatic monocarboxylic acids of not more than 4 carbon atoms from the higher boiling residues, and then subjecting this mixture to a further distillation to remove as distillate all the material present which in the presence of water is more volatile than formic and acetic acids.

The separation of the mixture of water and the aliphatic acids of 1 to 4 carbon atoms from the residues may, for example, be carried out by flash distillation without fractionating, or preferably with the provision of a certain degree of fractionation by means of a fractionating column and reflux. The separation may be carried out either under reduced pressure or at atmospheric pressure. The residues from this distillation may be oxidised or 105 recycled to the oxidation stages as for example as described in our copending Application No. 11469/53. It has generally been found desirable in this distillation to restrict the temperature of the still base to about 160° C. In this case it may be advisable to operate under 110 vacuum to obtain maximum stripping of acids.

According to another embodiment of the process of the present invention, the preliminary distillation of the oxidation product to remove volatile neutral oxidation products, may be carried out so as to remove only part of these products as a "light ends" fraction, the remainder being removed together with the neutral impurities whose removal from the acids is effected by the process of our invention by distillation of the mixture of water and

aliphatic acids of 1 to 4 carbon atoms, after separation thereof from the higher boiling residues.

According to another embodiment of the process of the present invention, the distillate obtained by the distillation of the mixture of water and aliphatic acids of 1 to 4 carbon atoms, after separation from residues, which normally separates into 2 liquid phases, may 5 be separated so that all or part of the upper liquid phase is removed, any remainder being returned to the still as reflux; and all or part of the lower liquid phase is returned to the still as reflux, any remainder being removed.

10 Of the two distillate liquid phases, the upper phase contains the bulk of the impurities whose removal from the acids is the object of our invention; these however may with advantage be recycled to the oxidation stage. The lower 15 liquid phase of the distillate is mainly water, and part or all of this may desirably be removed from the system since in this way a certain degree of dehydration may be achieved.

It is important, however, that there should 20 at all times be a sufficient concentration of water left in the base of the still at this stage to ensure complete removal of the impurities, and any dehydration effected should not be carried out so as to reduce the concentration of water in the base product to below 25 about 8-10% by weight.

The following examples are given to illustrate the process of the present invention:—

EXAMPLE 1.

35 An oxidation product, obtained by the liquid phase oxidation of a paraffinic hydrocarbon fraction of boiling range 15°-95° C., was fractionally distilled to remove the light ends completely. The base product from this 40 distillation was freed from the higher boiling compounds by distillation up a fractionating column packed with glass helices and equivalent to about 8 theoretical plates, at a reflux ratio of 1:1. The crude mixture of water and 45 the acids thus obtained was subjected to a further fractional distillation through a packed column up to a head temperature of 99° C. at atmospheric pressure which produced a further 1.0% by weight approximately of substantially 50 neutral material of a bright yellow colour which distilled over as a heteroazeotrope with water containing a small amount of acid. After removal of these impurities the remainder was fractionated up a column packed with glass helices, first in the presence of isopropyl ether 55 to remove water and then to separate a formic acid-acetic acid fraction. The formic acid-acetic acid fraction thus obtained was almost colourless and contained by analysis the following amounts of impurities:—

Ester—0.2 milliequivalents per 100 grams.
Carbonyl compounds—0.2 milliequivalents per 100 grams.

EXAMPLE 2.

60 An oxidation product similar to that used

in Example 1, was fractionally distilled to remove the light ends as completely as possible. The base product from this distillation was freed from the higher boiling components by distillation up a fractionating column 70 packed with glass helices and equivalent to about 18 theoretical plates, at a reflux ratio of 1:1. The crude mixture of water and acids thus obtained was subjected to a further fractional distillation through a packed column to 75 a head temperature of 99° C. at atmospheric pressure which produced a further 1.5% by weight of substantially neutral materials of a yellow colour distilling over as a heteroazeotrope with water containing a small amount of 80 acid. After removal of these impurities, the remainder was fractionated up a column packed with glass helices, first in the presence of isopropyl ether to remove water and then to separate a formic acid-acetic acid fraction. 85 The pure formic acid-acetic acid fraction thus recovered was colourless and contained no detectable ester or carbonyl impurity.

EXAMPLE 3.

An oxidation product similar to that used in 90 Example 1 was fractionally distilled in a continuous still at atmospheric pressure to remove the more volatile light ends, the head temperature being 60—65° C. The still base product was distilled at atmospheric pressure from 95 higher boiling material in a continuous still of about 30 theoretical plates with fractionation, the head temperature being about 100—110° C. The crude mixture of water and acid thus obtained was fed to the mid-point of a continuous 100 distillation column of 30 theoretical plates, under a reflux ratio of 7:1, the column head temperature being about 95° C. and the total distillate about 12% of the feed. The still base product from this distillation column 105 was dehydrated using isopropyl ether as the entrainer in a continuous still, and the dehydrated acids thus obtained were fractionally distilled in a batch still to recover the formic-acetic acid fraction. The formic acid 110 acetic acid fraction was colourless and contains no detectable ester or carbonyl impurity.

EXAMPLE 4.

An oxidation product obtained by the liquid phase oxidation of a paraffinic hydrocarbon 11° fraction of boiling range 15 to 95° C., was fractionally distilled to remove the volatile light ends in a continuous still. The still base product obtained was fractionally distilled to 12° separate the crude acids from the higher boiling material in a continuous still of 5 to 7 theoretical plates. The distillate comprising the aqueous aliphatic acids was fed to a continuous distillation column of approximately 15 theoretical plates, the reflux ratio being 12° about 9:1 and the head temperature 90 to 95° C., the total distillate being about 10% of the feed. The still base product obtained

was dehydrated in a continuous still using isopropyl ether as entrainer and the formic acid was then separated from the dried acids by entrainment with toluene in a continuous still. The base product thus obtained was fractionated through a continuous still to separate the acetic acid from the higher aliphatic acids and finally distilled to remove traces of toluene and formic acid. The acetic acid thus obtained was completely colourless, contained no detectable amounts of esters of ketonic compounds and completely satisfied the requirements of British Standard Specification, B.S. No. 576:1950.

15 By way of comparison a sample of the aqueous oxidate as used in Example 1 was fractionated in a fractionating column of about 15 theoretical plates packed with glass helices. The formic acid-acetic acid fraction of boiling point range 100-127/760 mm. mercury was 20 brown in colour and contained the following amount of impurities:—

Ester—16 milliequivalents per 100 grams.
Carbonyl compounds—17 milliequivalents per 100 grams.

After neutralisation with alkali a strong residual odour of higher ketones and esters remained.

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1 SHEET

COMPLETE SPECIFICATION
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